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[2] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710. J. S. Beck, J. C. Vartuli, W. L. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmidt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10 834.
[3] Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth, G. D. Stucky, *Nature* **1994**, *368*, 317.
[4] P. T. Tanev, M. Chibwe, T. J. Pinnavaia, *Nature* **1994**, *368*, 321. P. T. Tanev, T. J. Pinnavaia, *Science* **1996**, *271*, 1267.
[5] S. Mann, G. Ozin, *Nature* **1996**, *382*, 313.
[6] N. K. Raman, M. T. Anderson, C. J. Brinker, *Chem. Mater.* **1996**, *8*, 1682.
[7] M. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 7941.
[8] M. Ogawa, *Langmuir* **1995**, *11*, 4639. M. Ogawa, T. Igarashi, K. Kuroda, *Chem. Mater.* **1998**, *10*, 1382.
[9] M. Ogawa, *Chem. Commun.* **1996**, 1149.
[10] M. Ogawa, *Langmuir* **1997**, *13*, 1853.
[11] M. Ogawa, T. Igarashi, K. Kuroda, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2833.
[12] H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara, G. A. Ozin, *Nature* **1996**, *379*, 703. H. Yang, N. Coombs, I. Sokolov, G. A. Ozin, *J. Mater. Chem.* **1997**, *7*, 1285.
[13] H. Yang, N. Coombs, I. Sokolov, G. A. Ozin, *Nature* **1996**, *381*, 589.
[14] G. S. Attard, J. G. Glyde, C. G. Göltner, *Nature* **1995**, *378*, 366.
[15] I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger, S. M. Gruner, *Science* **1996**, *273*, 892. K. M. McGrath, D. M. Dabbs, N. Yao, I. A. Aksay, S. M. Gruner, *Science* **1997**, *277*, 552.
[16] H. W. Hillhouse, T. Okubo, J. W. van Egmond, M. Tsapatsis, *Chem. Mater.* **1997**, *9*, 1505.
[17] S. H. Tolbert, T. E. Schäffer, J. Feng, P. K. Hansma, G. D. Stucky, *Chem. Mater.* **1997**, *9*, 1962.
[18] Y. Lu, R. Gangull, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M. H. Huang, J. I. Zink, *Nature* **1997**, *389*, 364.
[19] M. T. Anderson, J. E. Martin, J. G. Odinek, P. P. Newcomer, J. P. Wilcoxon, *Microporous Mater.* **1997**, *10*, 13.
[20] J. E. Martin, M. T. Anderson, J. G. Odinek, P. P. Newcomer, *Langmuir* **1997**, *13*, 4133.
[21] A. Ayral, C. Balzer, T. Dabadie, C. Guizard, A. Julbe, *Catal. Today* **1995**, *25*, 219.
[22] T. Dabadie, A. Ayral, C. Guizard, L. Cot, P. Lacan, *J. Mater. Chem.* **1996**, *6*, 1789.
[23] M. Ferrer, P. Lianos, *Langmuir* **1996**, *12*, 5620.
[24] H.-P. Lin, C.-Y. Mou, *Science* **1996**, *273*, 765.
[25] Q. Huo, J. Feng, F. Schüth, G. D. Stucky, *Chem. Mater.* **1997**, *9*, 14.
[26] P. J. Bruishman, A. Y. Kim, J. Liu, S. Baskaran, *Chem. Mater.* **1997**, *9*, 2507.
[27] P. S. Singh, K. Kosuge, *Chem. Lett.* **1998**, 101.
[28] Q. Huo, D. Zhao, J. Feng, K. Weston, S. K. Buratto, G. D. Stucky, F. Schüth, *Adv. Mater.* **1997**, *9*, 974.
[29] S. A. Bagshaw, E. Prouzet, T. J. Pinnavaia, *Science* **1995**, *269*, 1242.
[30] R. Ryo, J. M. Kim, C. H. Ko, C. H. Shin, *J. Phys. Chem.* **1996**, *100*, 17 718.
[31] S. L. Burkett, S. D. Sims, S. Mann, *Chem. Commun.* **1996**, 1367.
[32] D. J. Macquarrie, *Chem. Commun.* **1996**, 1961.
[33] D. J. Macquarrie, D. B. Jackson, *Chem. Commun.* **1997**, 1781.
[34] M. H. Lim, C. F. Blanford, A. Stein, *J. Am. Chem. Soc.* **1997**, *117*, 4090.
[35] M. H. Lim, C. F. Blanford, A. Stein, *Chem. Mater.* **1998**, *10*, 467.

Optically Active Diarylethenes for Multimode Photoswitching Between Liquid-Crystalline Phases

By *Chagit Denekamp* and *Ben L. Feringa**

The control of the structure and optical properties of liquid-crystalline (LC) phases by means of light is a major challenge in the development of molecular device and optical data storage systems.[1] For instance the use of photochromic organic molecules for the modulation of mesophases is illustrated by the switching between nematic and isotropic LC phases based on the photochemical *cis–trans* isomerization of doped azobenzene in nematic media.[2]

It is well known that nematic liquid crystals can be converted into chiral nematic (induced cholesteric) LC materials using a chiral dopant.[3] Since nematic and chiral nematic LC phases exhibit distinct optical properties photochemical switching between these phases is highly significant for display technology. In a few cases reversible optical switching between a nematic (N) and chiral nematic (N*) phase has recently been demonstrated.[4–8] We have reported the photomodulation of LC phases using "chiroptical molecular switches".[5,8]

Photochemical interconversion of two opposite helices of *cis* and *trans* isomers of overcrowded alkenes doped in nematic LCs resulted in switching between two cholesteric phases, depending on the irradiation wavelength employed. As the isomers of the chiral dopant were pseudoenantiomers the pitches of the two phases were opposite in sign.[5] When enantiomers were used instead (racemic mixture), circular polarized light was necessary in order to achieve a small enantiomeric excess, which was amplified by doping the chiral overcrowded alkene photoswitch in a nematic LC phase, which resulted in a chiral nematic phase.[8] It is also conceivable that switching between nematic and cholesteric phases can be achieved by doping with a chiral photoswitch that exhibits large difference in twisting power in its two photostates.[4–7] By doping the nematic LC sample with the amount of dopant needed for the formation of a chiral liquid-crystalline phase only in one photostate a N $\rightarrow$ N* or N* $\rightarrow$ N LC switch can be produced.

Diarylethenes were found to be efficient optical switches (Scheme 1)[9–13] and the two photostates show very different absorption spectra (depending on the substituents). The absorption maximum of the closed-form diarylethene is about 300 nm red shifted from the absorption maximum of the open form, a feature that was used as a non-destructive read-out method. Chiral diarylethenes were shown to undergo asymmetric cyclization, providing one diastereo-

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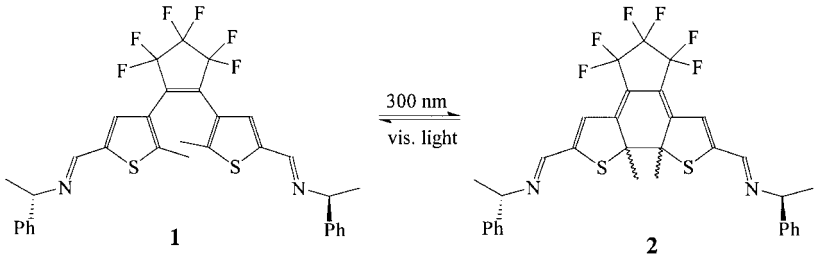
ADVANCED MATERIALS



Scheme 1. Photoisomerization of enantiomerically pure bisimine **1**.

mer in large excess.[13] In other cases it was found that even if the diastereomeric excess is almost zero the two states, that is, the open and the closed form, show very distinct circular dichroism (CD) and optical rotation dispersion (ORD) spectra.[14] We now wish to report the induction of chirality by doping diarylethene **1** in some nematic LCs and effective photomodulation of LC phases. Besides recording two different, wavelength-dependent, LC phases the gradual change in the pitch value as a function of irradiation time was investigated in order to illustrate multimode switching behavior.

The design of a suitable LC-compatible chiral optical switch is based on a bisimine-modified diarylethene-containing (*S*)-α-phenylethylamine appendage. The synthetic route, characterization, and photoisomerization of bisimine **1** are reported elsewhere.[14] Doping of nematic LC materials ZLI-389 and K_{15} with (*S*,*S*)-**1** resulted in stable cholesteric phases. In order to obtain a stable cholesteric phase in a large range of temperatures 2–4 wt.-% of **1** is required. It was possible, however, to induce a cholesteric phase with 0.7 wt.-% of **1** as long as the temperature was kept close to the transition temperature. When a mixture of **1** in ZLI-389 was heated under a microscope slide in a programmable hot stage and examined through crossed polarizers, a stable cholesteric phase was observed close to the N–I transition temperature.[15] When the temperature was kept within the range of 51–54 °C the cholesteric phase was stable for many hours (Fig. 1a). When the mixture of **1** in nematic LC ZLI-389 was irradiated with UV light of 300 nm for 50 s the chiral nematic phase disappeared and a nematic phase texture was observed (Fig. 1b).[16] Irradiation of the sample with visible light for 30 s resulted in the reappearance of the cholesteric fingerprint texture.

The switching cycle was performed 6 times without deterioration of the LC phases. The same experiment was repeated with K_{15} at 32 °C and photoswitching between the two states of chiral diarylethene dopant **1** resulted in change of the cholesteric phase to nematic (UV) and back to cholesteric (visible). From these results it is evident that the open form of chiral bisimine-substituted diarylethene, **1**, leads to the formation of a stable cholesteric phase both with ZLI-389 and K_{15}, while the helical twisting power of the closed form, **2**, is too low to effectively stabilize a cholesteric phase. The pitch and screw sense of the cholesteric phases and helical twisting power (HTP) were determined with the Grandjean–Cano technique (Table 1).[16,17]

Table 1. Pitch values, HTP, and handedness of the cholesteric phases formed by doping compound **1** in K_{15} and ZLI-389, as determined by the Cano–Grandjean method.

LC	wt.-% of **1**	Pitch [mm]	β_M [μm^{-1}]	Screw sense	Phase transition
ZLI-389	2.1	8.5	13	negative [a]	N* 54 I
K_{15}	2.1	12	11	negative	N* 33 I

[a] Doping with the enantiomer of **1** results in an opposite handedness.

The value of the pitch of the liquid-crystalline phases was measured independently by the droplet method and the same data were obtained (within 5 %).[18,19] After irradiation for 50 s with UV light of 300 nm no disclination lines were observed with the droplet method. Next a sample of

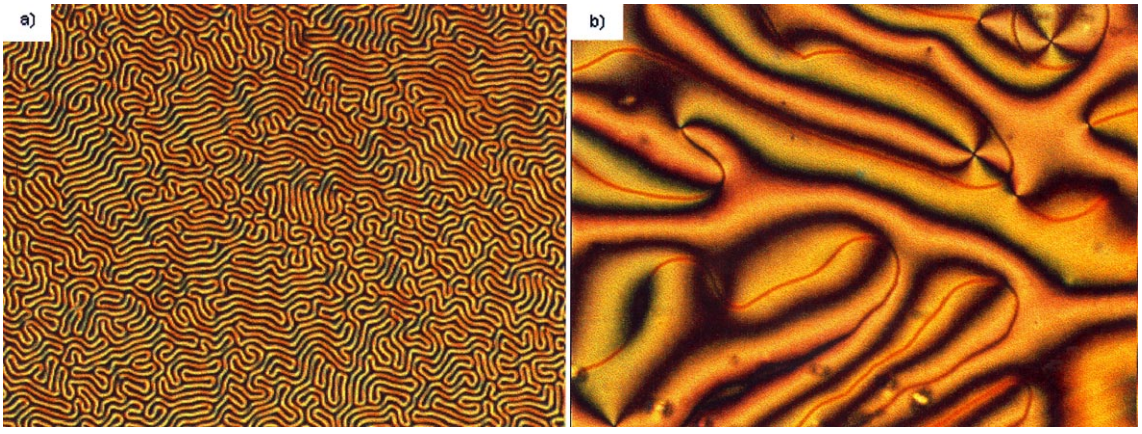


Fig. 1. The texture of the nematic and twisted nematic liquid-crystalline phases; 1.4 wt.-% of **1** in ZLI-389 52 °C. a) Cholesteric fingerprint texture. b) Nematic texture.

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ZLI-389 or K_{15}, doped with 2.0 % **1**, which was place between the glass slide and the lens used for the pitch determination, was irradiated with UV light of 300 nm and the change of the pitch with irradiation time was measured as shown in Figure 2. Under these conditions a pitch value could be determined even after long irradiation times for both doped LC phases (up to 30 min) since irradiation through the lens is less efficient. It was shown, however, that the pitch of the two twisted nematic LC phases can be gradually changed within irradiation time. These observations imply that in this case a multistate switch is demonstrated rather than a two-state switch as, depending on the irradiation time, a variety of states (with distinct *P*-values) can be addressed. The photochemical isomerization was reversible under these conditions as well: irradiation of the nematic LC phases (obtained by irradiation with UV light) with visible light for 10 min resulted in the reappearance of the cholesteric phase with the original pitch value.

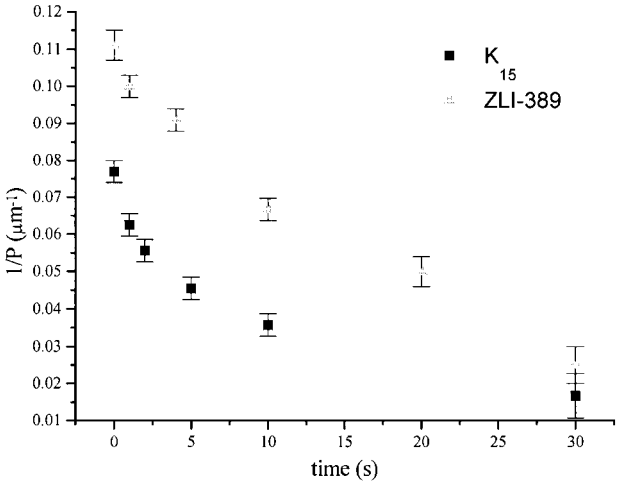

Fig. 2. The change of pitch value with irradiation time; 2.0 wt.-% of **1** in ZLI-389 at 52 °C and in K_{15} at 32 °C.

In conclusion, we have shown that the chiral diarylethene **1** can induce stable cholesteric phases when doped in the nematic LCs K_{15} and ZLI-389 and the switching between the two forms of dopant diarylethenes **1** and **2** results in the disappearance and reappearance of the cholesteric phase. An effective N → N* or N* → N switch is therefore produced. Moreover, the pitch can be gradually changed with irradiation time and as a consequence the basic features of a multimode LC switch are demonstrated.

The decrease in pitch value via isomerization of the open form diarylethene **1** to the closed form **2** indicates that the twisting power of **2** is considerably smaller then the twisting power of **1**. However, since **2** is a mixture of two diastereomers it is not clear at this moment to what extent the diastereomeric product ratio of **2** affects the twisting power and via a partial compensation effect influences the chirality of the liquid-crystalline phase.

In order to improve the switching rate[20] and modify the wavelength used for switching as well as the pitch value other diarylethylene derivatives are currently under investigation.

Experimental

The liquid-crystalline materials K_{15} (4′-pentyl-4-biphenylcarbonitrile) and the ZLI-389 mixture of methoxyphenylpentylbenzoate, hexyloxyphenylpentylbenzoate, and 4-butyl-2-cyano-1-(hexyloxyphenylcarbonyloxy)benzene were purchased from Merck (Darmstadt). The phase transitions were determined by polarization microscopy using an Olympus BX 60 microscope and a Linkam THMS 600 hot stage. Irradiation was performed with a coated 8 W low pressure mercury lamp at 300 nm, and a 150 W tungsten lamp was used for visible light. The converging lenses for determination of the pitch were purchased from Steeg & Reuter, Germany, and the polyamide (Licralign CU1511) for surface alignment from Merck, Darmstadt [16]. Glycerol was used for the determination of the pitch by the droplet method [19].

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[1] D. Kreysig, J. Stumpe, in *Selected Topics in Liquid Crystalline Research* (Ed: H. D. Koswig), VCH, Weinheim **1990**.
[2] a) T. Ikeda, O. Tsutsumi, *Science* **1995**, *268*, 1873. b) T. Ikeda, T. Sasaki, K. Ichimura, *Nature* **1993**, *361*, 428.
[3] G. Solladie, R. G. Zimmermann, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 348.
[4] E. Sackmann, *J. Am. Chem. Soc.* **1971**, *93*, 7088.
[5] B. L. Feringa, N. P. M. Huck, H. A. Van Doren, *J. Am. Chem. Soc.* **1995**, *117*, 9929.
[6] T. Yokoyama, S. Toshiya, *Chem. Lett.* **1997**, 687.
[7] S. Z. Janicki, G. B. Schuster, *J. Am. Chem. Soc.* **1995**, *117*, 8524.
[8] N. P. M. Huck, W. F. Jager, B. de Lange, B. L. Feringa, *Science* **1996**, *273*, 1686.
[9] M. Irie, M. Mohri, *J. Org. Chem.* **1988**, *53*, 803.
[10] M. Hanazawa, R. Sumiya, Y. Horikawa, M. Irie, *J. Chem. Soc., Chem. Commun.* **1992**, 206.
[11] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, *J. Org. Chem.* **1995**, *60*, 8305.
[12] S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275.
[13] T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **1997**, *119*, 6066.
[14] B. L. Feringa, C. Denekamp, unpublished.
[15] The N–I transition temperature at which the phase transition from nematic liquid-crystalline phase to isotropic liquid phase occurs. The transition temperature is noted in the following manner: N *t* I where *t* is the temperature.
[16] The distances between the concentric rings of Grandjean–Cano lines were measured using a converging lens with planar boundary conditions. To provide a concentric planar surface alignment both the converging lens and the microslide are rubbed unidirectionally, after having been coated with polyamide. The pitch is the distance between two lines and can be calculated by $(r_{n_2} - r_{n_1})^2/R$ where r_{n_1} and r_{n_2} are the radii of the Grandjean–Cano circles and R is the radius of the lens. D. Demus, L. Richter, *Textures of Liquid Crystals*, Verlag Chemie, Weinheim **1978**.
[17] a) R. Cano, *Bull. Soc. Fr. Mineral.* **1968**, *91*, 20. b) F. C. R. Granjean, *Hebd. Seances Acad. Sci.* **1921**, *172*, 71.
[18] S. Candau, P. L. Roy, F. Debeauvais, *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 283.
[19] The doped LC was mixed with glycerol and the mixture was placed between two microslides. The distance between two concentric rings in the drops is half the pitch.
[20] As suggested above irradiation through the lens is less efficient. It is also reasonable to assume that the photochemical switching reaction can be made faster if instead of a tungsten lamp a monochromatic, intense light is used as a visible light source.

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